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Article

Design, Synthesis, and Tribological Behavior of An Eco-friendly Methylbenzotriazole-Amide Derivative

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Abstract: Benzotriazole and its derivatives show good tribological properties, anti-oxidation, anti-corrosion, rust prevention and dispersion capabilities as lubricating additives, becoming the common multifunctional additives. And how to avoid sulfur- or phosphorus-introduction to improve their functionality and the compatibility with hydrocarbons is the forefront research. In this study, methylbenzotriazole and oleic acid were applied to synthesize a new methylbenzotriazole-amide that with long alkyl-chain (E)-N-(2-(5-methyl-2H-benzodiazole-2-yl)ethyl)octadec-9-enamide (MeBz-2-C18), which was characterized by nuclear magnetic resonance (NMR), high-resolution mass spectrometry (HR-MS), FT-IR and thermogravimetric analysis (TGA). The thermal stability and tribological properties of MeBz-2-C18 were compared with the commercially available benzotriazole oleamide (T406). The results show that MeBz-2-C18 has better thermal stability and base oil compatibility than that of T406, and 0.5 wt.% addition of MeBz-2-C18 could decrease the average wear scar diameter (ave. WSD) by 21.6%. The wear surface analysis and DFT calculation show that the amide group in MeBz-2-C18 is preferentially broken during friction, which would reduce the interfacial shear force and easily react with the metal surface to form iron oxide film, thus demonstrating a better anti-wear and friction reducing performance, indicating its potential application as an environmental friendly multifunctional additive.

Keywords: multifunctional additive; methylbenzotriazole; amide derivative; synthetic hydrocarbon; tribological behavior

1. Introduction

Before the 1930s, straight-run mineral oils were sufficient to meet the demands of machinery operation. However, with the upgrade of mechanical equipment, especially the improvement of engine power, more stringent requirements were put forward for the performance of lubricants, which triggered additive researches and thus lubricants entered the additive era.[1]

Many studies have shown that nitrogen-containing heterocyclic compounds are applied in various additives due to their dense chemical structures, good thermal stability, easy to adsorb on metal surfaces and prevent corrosion[2-5]. These compounds can enhance the extreme pressure, anti-wear and friction-reducing properties of base oils. Moreover, the abundant nitrogen can form efficient protective films during friction and be absorbed by microorganisms as a primary nutrient after use, contributing to their biodegradability[6–8]. Benzotriazole and its 0derivatives, in particular, exhibit excellent tribological properties along with anti-oxidation, anti-corrosion[9], rust prevention[10], and dispersion capabilities[11], making them common multifunctional additives.

Liu et al.[12] investigated the corrosion inhibition mechanisms of several types of triazole derivatives on copper surfaces. They found that the lone pairs of electrons in empty orbitals of O and

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N atoms for triazole derivatives can hybridize with the d-orbitals of Cu atoms to form covalent bonds through theoretical calculations, which enhanced the adsorption and passivation effect on copper surfaces, thus achieving corrosion inhibition, friction and wear reducing properties. Li et al.[13] replaced the metal ions in dialkyldithiophosphates with benzotriazole groups to synthesize a sulfur- and phosphorus-containing benzotriazole derivative (BDDP), which exhibited good extreme pressure and friction-reducing properties in rapeseed oil.

However, with the development of sustainable development concept and the understanding of green chemistry, researchers began to focus on non-metallic and environmental friendly additives that only contain carbon, hydrogen, oxygen, nitrogen, boron, etc. In 2009, Xiong[14] synthesized a novel sulfur- and phosphorus-free benzotriazole derivative, and its tribological properties were evaluated in hydrogenated base oil. The results showed that it not only improved the load-carrying capacity and friction-reducing properties, but also exhibited good synergistic effects with tricresyl phosphate. He[15] prepared a sulfur- and phosphorus-free benzotriazole alcohol compound, and the maximum non-seizure load (PB) of the base oil increased (441.3 N to 607.6 N) significantly with its increasing addition (0 to 2.0 wt.%).

Although benzotriazole derivatives exhibited good tribological properties as lubricating additives, their poor solubility in hydrocarbons limited applications, so researchers began to improve the oil solubility. Li[16] synthesized a methylbenzotriazole fatty amine salt using methylbenzotriazole and fatty amine, which was compared with commercially available benzotriazole fatty amine salt in base oil (150N). The results revealed that the methylbenzotriazole fatty amine salt exhibited better oil solubility than that of commercial available product, while both of them showed comparable tribological performance, which suggests that methylbenzotriazole can serve as a suitable substitute for benzotriazole to improve its compatibility with base oils. Xu[17] used 1,3-diamino-2-propanol and oleic acid to synthesize 1,3-dioleoamide-2-propyloleate (DOAPO), which combined polar amide, ester and nonpolar alkyl chains. Their study showed that DOAPO exhibited good thermal stability and storage stability in synthetic hydrocarbons. The tribological tests showed that 0.5 wt.% addition of DOAPO could shorten the running-in period and reduce the ave.COF and ave.WSD by 8.2% and 16.2%, respectively.

In this study, a green lubricating additive (E)-N-(2-(5-methyl-2H-benzo[d][1,2,3]triazol-2-yl)ethyl)octadec-9-enamide (MeBz-2-C18) with alkyl chain and amide as functional groups was designed and synthesized using methylbenzotriazole framework (5-methyl-1H-benzo[d][1,2,3]triazole). The synthesized compound was characterized by NMR, HR-MS, FT-IR and TGA, and the storage stability and tribological performance in low-viscosity synthetic base oils were compared with the commercially available T406 Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analysis of the worn surfaces, combining DFT theoretical calculations, were used to elucidate the micro-lubrication mechanism of MeBz-2-C18.

2. Results

2.1. Synthesis of MeBz-2-C18

The MeBz-2-Etn was first synthesized through a substitution reaction between 2-chloroethylamine and 5-methylbenzotriazole, which was reacted directly with oleoyl chloride to prepare the amide compound MeBz-2-C18. The synthesis pathway is illustrated in Scheme 1.

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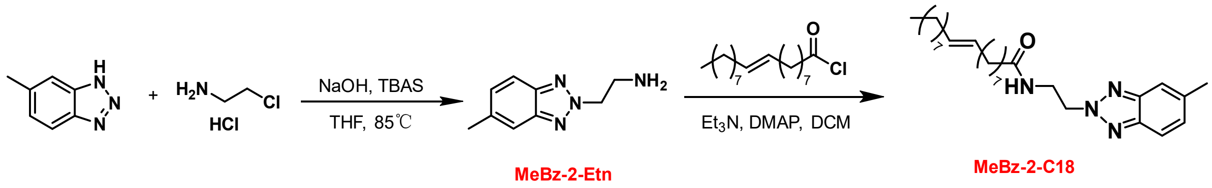

Scheme 1. The synthesis route of MeBz-2-C18**.**

NMR, HR-MS and FT-IR were used to determine the structure of MeBz-2-C18, and the results are presented in Section 3.2. Figure 1 compared the ^{1}H NMR spectra of MeBz-2-Etn and MeBz-2-C18. In MeBz-2-C18, hydrogen signals of oleoyl alkyl with chemical shifts at 2.13, 2.01, 1.55, 1.26, 0.88 ppm and -CH=CH- with a chemical shift at 5.34 ppm appeared. Meanwhile, the -CH_2 directly connected to -NH underwent a significant downfield shift (from 3.36 ppm to 3.93 ppm) due to the introduction of C=O. As can be observed from FT-IR spectra in Figure 2, compared with MeBz-2-Etn, there is no N-H stretching vibrations of primary amine at 3372.9 and 3295.8 cm^{-1} in MeBz-2-C18. However, the C=O(NH) characteristic stretching vibration of secondary amide appears at 1643.5 cm^{-1}, and the N(CO)-H and C(O)-N(H) stretching vibration peaks of secondary amide appear at 3309.7, 3071.7 and 1265.1 cm^{-1}, respectively. Moreover, the peak located at 721.8 cm^{-1} can be attributed to the in-plane bending vibration of long alkyl chain -$(CH_2)_n$-. Collectively, these spectral characteristics serve as evidence for the successful grafting of oleoyl group in MeBz-2-C18.

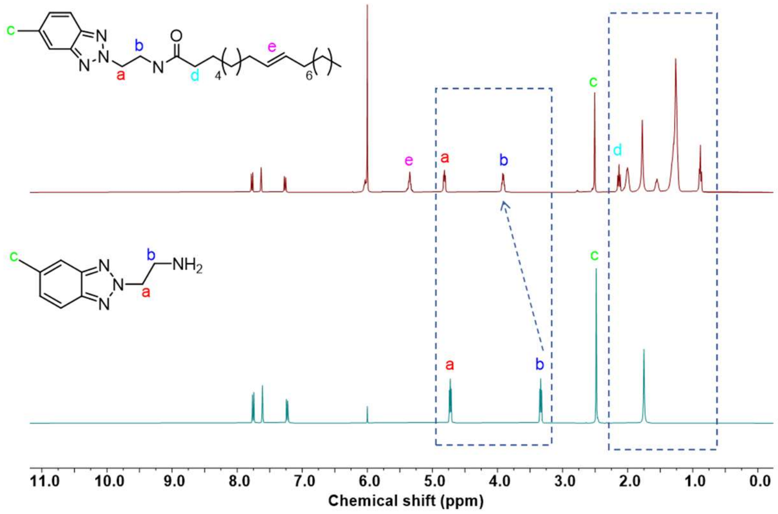

Figure 1. H NMR spectra of MeBz-2-Etn and MeBz-2-C18.

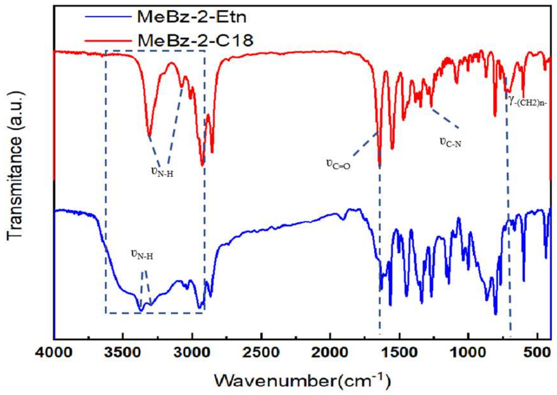

Figure 2. FT-IR spectra of MeBz-2-Etn and MeBz-2-C18.

2.2. Stability Characterization

2.2.1. Thermal Stability

Thermal stability serves as a crucial determinant in the lifespan of additives, which is an important guarantee for additives. In this regard, a comparative investigation was carried out on the thermal stabilities of MeBz-2-Etn, MeBz-2-C18 and the commercially available T406. According to the analysis of the thermogravimetric curves in Figure S3 and Table 1, the initial decomposition temperatures of T406, MeBz-2-Etn, and MeBz-2-C18 were measured to be 76.8 °C, 19.7 °C and 185.5 °C, while the maximum decomposition temperatures were determined as 221.1 °C, 217.4 °C and 374.4 °C, demonstrating that the thermal stabilities can be ranked as MeBz-2-C18 > T406 > MeBz-2-Etn in descending order. Furthermore, in comparison with T406, the residual masses of MeBz-2-C18 at 200 °C and 300 °C were found to be 99.9%, 79.9% and 89.3%, 11.0% respectively, which indicates that the incorporation of ethylamine contributes to the thermal stability enhancement of additives.

Table 1. Thermal stability analysis of MeBz-2-Etn、MeBz-2-C18 and T406.

Item		**MeBz-2-Etn**	**MeBz-2-C18**	**T406**
Decomposition temperature (°C)	Initial	19.7	185.5	76.8
	Max.	217.4	374.4	221.1
	Terminal	236.0	434.7	420.3
Residual mass (%)	@ Max. decomposition	15.1	22.4	39.2
	@200 °C	44.8	99.9	71.9
	@300 °C	1.8	89.3	11.0
	@400 °C	1.0	1.3	1.3

2.2.2. Storage Stability in Base Oil

The compatibility between additives and base oils is a decisive factor in the storage stability of lubricating oils, which also serves as a fundamental prerequisite for their practical applications. Therefore, the compatibility of different MeBz-2-C18 additions with the base oil were studied, and the stability of oil samples with the same concentration of the commercially available T406 was compared. As shown in Figure 3 and Table S1, the oil samples with 0.25-1 wt.% additions of MeBz-2-C18 remained clear and transparent after being stored at room temperature for 30 days (Figure 3a). In contrast, the oil sample with 0.5 wt.% T406 became cloudy on the 7th day (Figure 3b), demanstrating that the compatibility of MeBz-2-C18 with the base oil is better than that of T406.

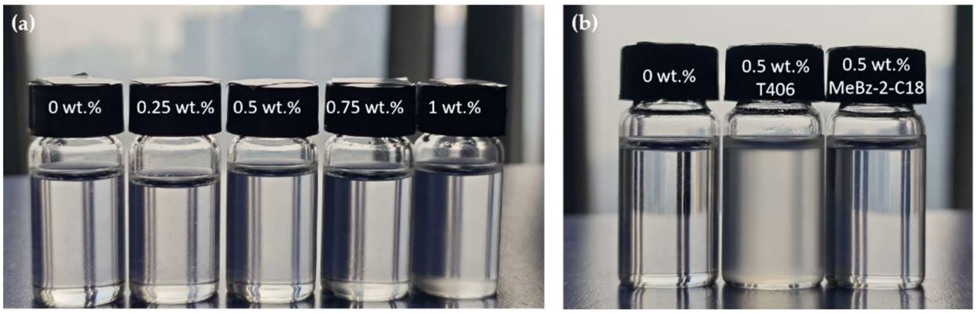

Figure 3. Appearance of oil samples with (**a**) different additions of MeBz-2-C18 after 30 days; (**b**) the same addition (0.5 wt.%) of MeBz-2-C18 or T406 after 7 days.

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2.3. Tribological Behaviors

2.3.1. Different Additions of MeBz-2-C18

As for lubricating oils, their performance often varies with different additive additions, and the optimal addition can endow oils with the best overall performance. Figure 4 shows the tribological performance of oil samples with different MeBz-2-C18 additions. It can be seen from Figure 4a that there are significant differences in the friction curves between the base oil (0 wt%) and oil samples with MeBz-2-C18. The friction running-in period of the base oil is long (~300 s), and the coefficient of friction (COF) in the relative-stable period fluctuates significantly. In contrast, the oil sample with 1 wt% MeBz-2-C18 has a shorter running-in period (~200 s), and the COF is more stable and much smaller. A further comparison in Figure 4b shows that the oil with 0.5 wt.% MeBz-2-C18 has the smallest ave. WSD, which is decreased by 21.6% compared to that of the base oil, and its ave.COF reduces by 3.2%. The oil with 1 wt.% MeBz-2-C18 reveals a lowest ave. COF, which is reduced by 8.4% compared to that of the base oil, and the ave. WSD is decreased by 13.9%. Overall, the oil with 0.5 wt.% MeBz-2-C18 exhibits the best tribological performance compared to the base oil.

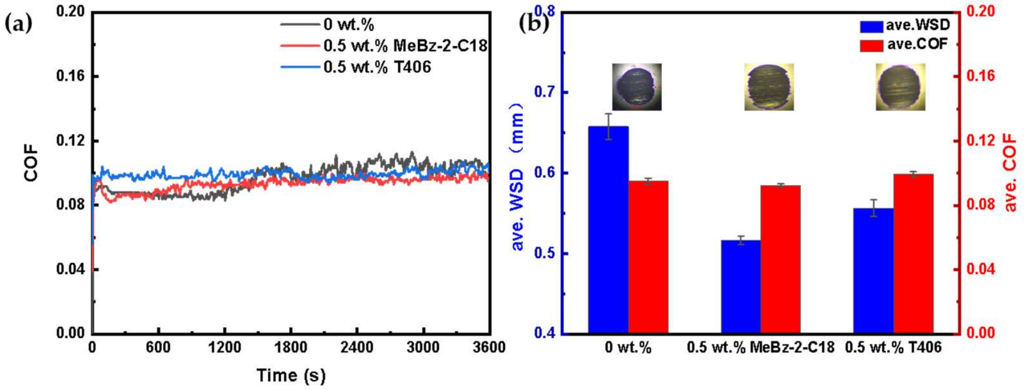

Figure 4. a) Friction profiles and (**b**) ave. COF and ave. WSD of oil samples with different additions of MeBz-2-C18.

2.3.2. Comparison with Commercial Additive

The tribological performance of MeBz-2-C18 was compared with the commercially available additive T406, using 0.5 wt.% as the optimal addition. As shown in Figure 5a, the COF of the base oil suddenly increased and significant fluctuations occurred after 1200 s during the friction. However, the COF of the oils with 0.5 wt.% T406 or MeBz-2-C18 showed smaller variations, indicating that the addition of T406 and MeBz-2-C18 could stabilize the friction. According to the comparison results of ave. COF and ave. WSD in Figure 5b, compared with the base oil, the ave. COF and ave. WSD of the oil with 0.5 wt.% MeBz-2-C18 decreased by 3.2% and 21.6% respectively. While the ave. WSD of oil with 0.5 wt.% T406 was decreased by 13.9%, but its ave. COF increased by 4.5%, which indicating that MeBz-2-C18 exhibits better tribological performance than that of T406.

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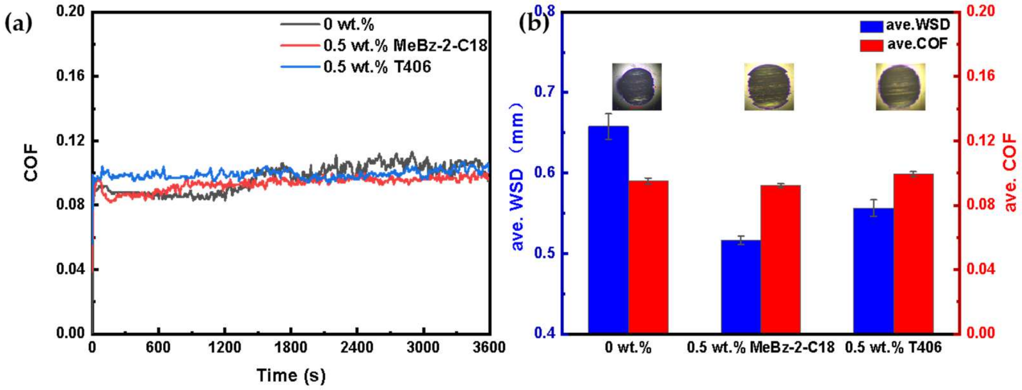

Figure 5. a) Friction profiles, (**b**) ave. WSD and ave. COF of oils with 0.5 wt.% of additives.

2.4. Lubrication Mechanism

2.4.1. Wear Surface Analysis

To investigate the micro-lubrication mechanism of as-prepared methylbenzotriazole-amide compound in the synthetic base oil, SEM-EDS and XPS were employed to analyze the composition of friction films on the worn surface and non-worn surface of oil samples containing 0.5 wt.% MeBz-2-C18 (designated as MeBz-2-C18-Non-wear and MeBz-2-C18-wear, respectively). These were compared with the worn surface of the base oil (Base oil-wear).

The results of the analysis on morphologies and elemental compositions are presented in Table S2. It can be observed from the SEM images that the metal surface lubricated with the base oil experiences more severe wear compared to that lubricated with the oil containing 0.5 wt.% MeBz-2-C18, suggesting that MeBz-2-C18 can enhance the anti-wear performance of the synthetic base oil. According to EDS analysis, the Fe, C and O contents of the non-wear and wear surfaces lubricated with the base oil are 69.95%, 22.54%, 7.51% and 45.97%, 25.57%, 28.46%, respectively. While the Fe content of the non-wear and wear surfaces lubricated with oil containing 0.5 wt.% MeBz-2-C18 are 63.86% and 35.62%, which is lower than that lubricated with the base oil. The C and O contents of the non-wear and wear surfaces lubricated with oil containing 0.5 wt.% MeBz-2-C18 are 27.57%, 34.24% and 8.58%, 30.14% which is higher than those lubricated with the base oil, indicating that MeBz-2-C18 participates in the formation of friction films.

XPS was used to compare the bonding states of elements before and after tribological tests, which can provide valuable information about the chemical changes that occur during friction[18]. Figure 6 and Table S3 display the deconvolution analysis of C, O, Fe and N bonding states for the wear surfaces lubricated with base oil and oil containing 0.5 wt.% MeBz-2-C18. In C1s spectra, there are four main peaks for MeBz-2-C18_wear, namely metal carbides (283.4 eV, ~2.9%), C-C/C=C (284.8 eV, ~72.9%), C-O/C-N (286.0 eV, ~20.4%) and C=O (288.5 eV, ~3.6%)[19-20]. In contrast, the Base oil-wear spectrum only exhibits C-C/C=C (284.8 eV, ~86.9%) and C-O/C-N (286.0 eV, ~13.1%). In O1s spectra, peaks at 529.6 eV, 531.7/531.9 eV and 533.1 eV correspond to Fe-O, C=O and C-O bonds, respectively. Notably, the content for C=O in MeBz-2-C18_wear increases compared to that of Base oil-wear, indicating that the amide bonds were broken during friction, which further led to the formation of carbonyl compounds., The peaks at 709.6 eV, 723.5 eV, 713.5 eV and 711.0 eV in Fe2p spectra correspond to Fe (2p3/2), Fe^{2+} (2p1/2), Fe^{2+} (2p3/2) and Fe^{3+} (2p3/2), respectively. This suggests that local high temperatures and high loads caused chemical reactions between iron in steel balls and oxygen in air during friction[21-22]. Combined with the O1s spectra, it is evident that an iron oxide film was formed during friction, which might be composed of Fe_2O_3, FeOOH, FeO and Fe_3O_4[23]. Additionally, the N1s peaks for MeBz-2-C18_wear appear at 399.4 eV and 401.7 eV, corresponding to N-O and C-N bonds, which indicates that some amides were converted into nitrogen oxides[24-25].

The results demonstrate that the friction film formed by MeBz-2-C18 consists of organic oxides and iron oxides, which can enhance the anti-wear and friction-reducing properties.

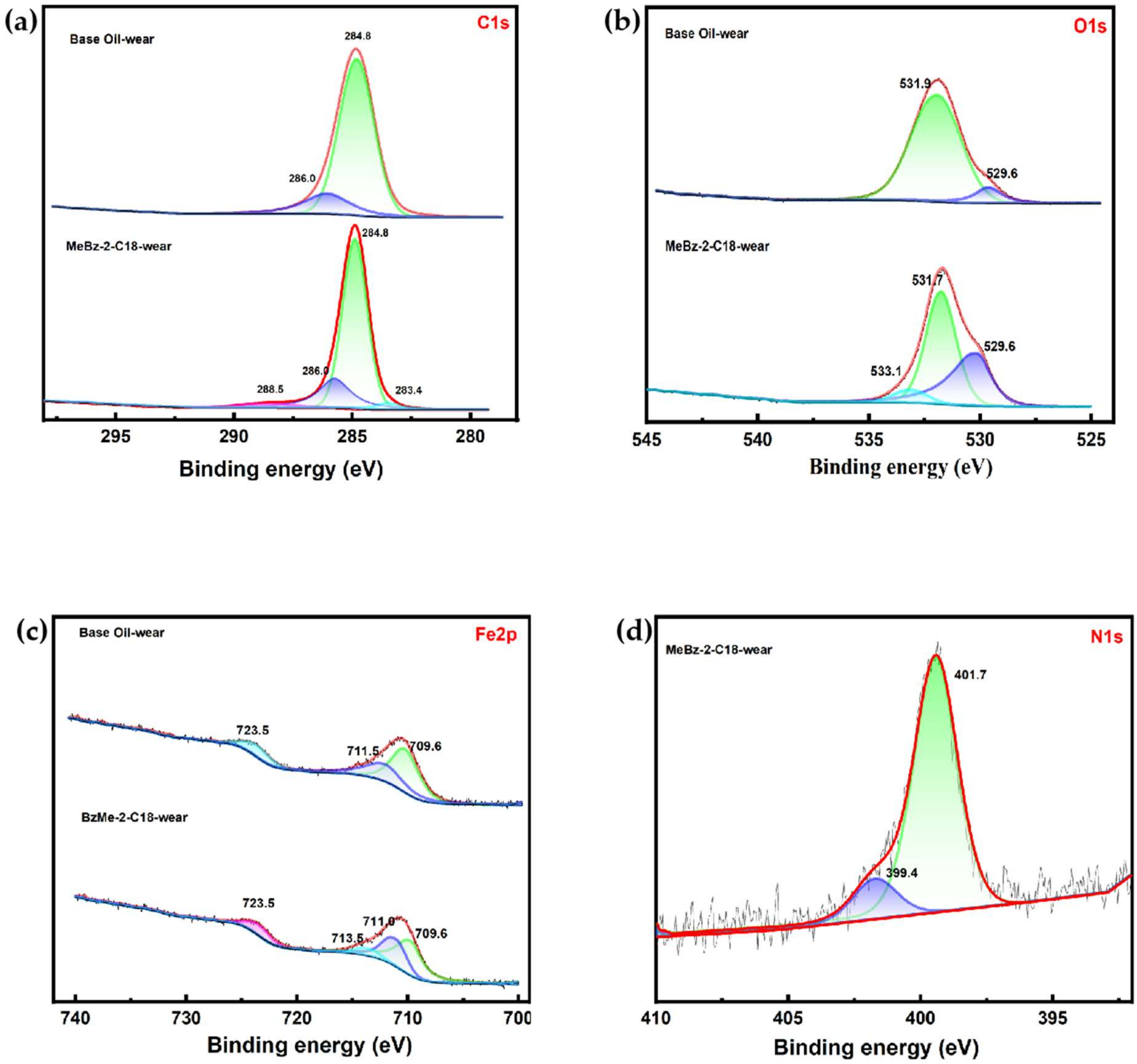

Figure 6. Worn surface analysis of base oil and oil with 0.5 wt.% MeBz-2-C18 by XPS spectra: (**a**) C1s; (**b**) Fe2p; (**c**) O1s; (d) N1s.

2.4.2. DFT Calculations

To investigate the structure impact on the tribological performance of lubricants, DFT calculations were performed using Gaussian16 software to analyze the electrostatic potential (ESP). The B3LYP hybrid functional was employed for the geometric optimization of MeBz-2-C18 and T406, and the ESP of C, H, O and N atoms was analyzed using the 6-31G(d) basis set. The optimized structures were characterized by harmonic vibrational frequencies, identified as minima (Nimag = 0) or transition states (Nimag = 1). The electronic energy spectrum of the compounds was calculated using Multiwfn, defining the molecular surface as an isosurface of electron density r = 0.001 a.u. As shown in Figure.7, the minimum ESP values for T406 and MeBz-2-C18 are -0.0475 and -0.0665, while the maximum ESP values are 0.0565 and 0.0731, indicating that MeBz-2-C18 has a stronger adsorption capability on metal surfaces compared to T406. This strong adsorption characteristic is consistent with the results of the previous tribological tests, that is, the friction-reducing and anti-wear

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performances of MeBz-2-C18 are better than those of T406. XPS analysis show that the amide bonds in MeBz-2-C18 would break during friction, which is conducive to its reaction with the metal surface and then the formation of a metal oxide film, thus playing an anti-wear role. In addition, the breaking of amide bonds reduces the interfacial shear force and improves the friction-reducing performance. Overall, MeBz-2-C18 can not only form a strong adsorption film on the metal surface but also generate chain scission during friction, optimizing its tribological performance.

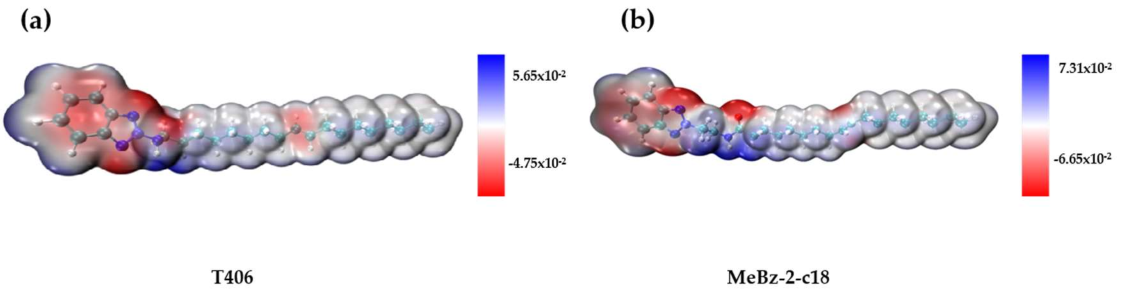

Figure 7. Theoretical electrostatic potential (ESP) calculation of (**a**) T406 and (**b**) MeBz-2-C18.

Combined DFT calculations and wear surface analysis, MeBz-2-C18 exhibits stronger adsorption on metal surfaces compared to the commercial T406 (ESP: -0.0665 vs. -0.0475). During friction, the amide bonds in MeBz-2-C18 are more likely to break, generating polar amine groups and alkyl chains, as depicted in Figure 8. This chain scission reduces interfacial shear forces, and the oxygen atoms produced react with the metal surface to form an iron oxide protective film. Moreover, the benzimidazole can coordinate with the metal, which enables MeBz-2-C18 to exhibit excellent anti-wear and friction-reducing properties.

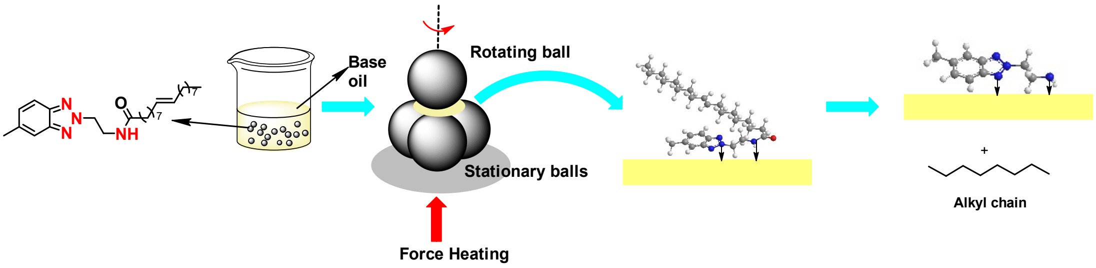

Figure 8. Schematic diagram of the lubrication mechanism with MeBz-2-C18**.**

3. Materials and Methods

3.1. Materials

5-Methylbenzotriazole (98%) was obtained from J&K Scientific (Beijing, China). Chloroethylamine hydrochloride (98%) and 4-dimethylaminopyridine (DMAP, 99%) were sourced from Beijing InnoChem Science & Technology Co., Ltd. (Beijing, China). Tetrabutylammonium bisulfate (TBAS, 99%) and oleoyl chloride (89%) were purchased from EnergyChemical (Shanghai, China). Sodium hydroxide (NaOH) and triethylamine (Et_3N, 99.9%) were acquired from Shanghai Laboratory Reagent Co., Ltd. (Shanghai, China). Dichloromethane (DCM, 99.9%) was supplied by Shanghai Titan Technology Co., Ltd. (Shanghai, China), and tetrahydrofuran (THF, 99.9%) was obtained from Changshu Hongsheng Fine Chemical Co., Ltd. (Changshu, China).

Durasyn®164 (PAO4, INEOS, London, UK) and Priolube 3970 (3970, CRODA, Snaith,UK) were separately purchased from Shanghai Qicheng Industrial Co., Ltd. (Shanghai,China) and Hersbit Chemical Co., Ltd. (Shanghai, China), which were applied as base oils for the tribological evaluation of MeBz-2-C18 and T406 (Suzhou Xingchangrun Chemical Co., LTD) was used as a commercial additive to compare with MeBz-2-C18.

3.2. Synthesis of MeBz-2-C18

5-Methylbenzotriazole (10.00 g, 75.18 mmol), NaOH (9.02 g, 225.54 mmol), and THF (150 mL) were mixed in a flask and reacted at room temperature for 30 minutes. Then, 2-chloroethylamine hydrochloride (13.08 g, 117.77 mmol) and TBAS (1.06 g, 3.13 mmol) were added, followed by heating and refluxing for 12 hours. The reaction was monitored by TLC until the complete conversion of 5-methylbenzotriazole was achieved. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in DCM and washed with saturated NaCl solution. The organic phase was extracted with DCM, dried, and the crude product was purified by column chromatography (eluent: V_{DCM}/V_{MeOH} = 7:1), yielding 5-methylbenzotriazole-2-ethylamine (4.37 g, yield 33%), which was obtained as a colorless oily liquid and referred to as MeBz-2-Etn.

^{1}H NMR (400 MHz, Tetrachloroethane-d2) δ 7.75 (d, J = 8.7 Hz, 1H), 7.61 (s, 1H), 7.23 (d, J = 10.2 Hz, 1H), 4.76-4.69 (m, 2H), 3.36-3.31 (m, 2H), 2.48 (s, 3H), 1.75 (s, 2H) (Figure S1a). ^{13}C NMR (101 MHz, Tetrachloroethane-d_2) δ 144.90, 143.02, 136.75, 129.45, 117.52, 116.38, 74.34, 74.06, 73.79, 59.45, 42.05, 22.25 (Figure S1b). HR-MS (ESI) calcd. for $C_9H_{13}N_4$ $[M+H]^+$: 117.11328,found: 117.11328 (Figure S1c). FT-IR (ATR): ν =3369.7, 3034.8, 2945.6, 2866.9, 1904.8, 1563.3, 1448.8, 732.0, 598.1 cm^{-1} (Figure S1d).

Subsequently, 5-methylbenzotriazole-2-ethylamine (4.5 g, 25.57 mmol), DMAP (0.3 g, 2.56 mmol), and Et_3N (6.47 g, 63.93 mmol) were mixed in anhydrous DCM (90 mL) in a flask under an argon atmosphere. Oleoyl chloride (11.54 g, 38.36 mmol) was slowly added at 0°C. The mixture was then allowed to react at room temperature for 12 hours. TLC monitoring confirmed the complete conversion of 5-methylbenzotriazole-2-ethylamine, and the reaction was quenched with water. The mixture was washed with saturated $NaHCO_3$ and NaCl solutions, and the organic phase was extracted with DCM and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (eluent: V_{PE}/V_{EA} = 1:1), yielding (E)-N-(2-(5-methyl-2H-benzo[d][1,2,3]triazol-2-yl)ethyl)octadec-9-enamide as a pale yellow solid (10.79 g, yield 96%), referred to as MeBz-2-C18.

^{1}H NMR (400 MHz, Tetrachloroethane-d_2) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.63 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 6.06-6.02 (m, 1H), 5.34 (s, 2H), 4.85-4.79 (m, 2H), 3.93-3.89 (q, *J* = 5.7 Hz, 2H), 2.51 (s, 3H), 2.13 (t, *J* = 7.6 Hz, 2H), 2.01 (s, 4H), 1.55 (m, 2H), 1.26 (s, 20H), 0.88 (t, *J* = 6.7 Hz, 3H) (Figure S2a). ^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ 173.53, 144.93, 143.06, 136.96, 130.20, 129.98, 129.64, 117.55, 116.40, 74.33, 74.05, 73.78, 55.70, 38.99, 36.66, 32.05, 29.92, 29.87, 29.68, 29.47, 29.40, 29.29, 29.26, 27.36, 27.33, 25.66, 22.88, 22.27, 14.40 (Figure S2b). HR-MS (ESI) calcd. for $C_{27}H_{44}N_4ONa$ $[M+Na]^+$: 463.34073, found: 463.34073 (Figure S2c). FT-IR (ATR): ν =3307.4, 3071.4, 2922.3, 2851.4, 1638.9, 1465.9, 721.8, 597.9 cm^{-1} (Figure S2d).

3.3. Characterizations

NMR characterization, including ^{1}H NMR and ^{13}C NMR, was conducted on a 400-MR (Varian, Palo Alto, CA, USA) using d-TCE as the solution. HR-MS was carried out on JMS-T100LPAccuTOF LC-plus 4G (Nippon Electronics Corporation, Tokyo, Japan) using electrospray ionization. Nicolet iN10MX (Thermo Fisher, Waltham, MA, USA) was applied to record FT-IR spectroscopy by scanning from 400 to 4000 cm^{-1}. TGA was performed on Q500 (TA, Milford, MA, USA) under a N_2 atmosphere with a flow rate of 60 mL/min and a heating rate of 10 °C/min from 25 to 600 °C. The morphology and elemental composition of metal surfaces are analyzed by SEM-EDS using QUANTAX (Bruker, San Jose, CA, USA). The chemical state of specific elements and potential tribochemical films formed on the frictional surface were analyzed using XPS, (Thermo Scientific K-Alpha, Waltham, MA, USA) with an Al-Kα radiation source, and the obtained spectra were analyzed using the Avantage 5.9931 software.

3.4. Preparation of Oil Samples

The synthetic hydrocarbon PAO4 (90 wt.%) and saturated polyol ester 3970 (10 wt.%), which are both low viscosity, were blended after heating and stirring at 60 ℃ for 2 h to obtain the mixed base oil. Oil samples containing additives were prepared as follows: 0 ~ 1.0 wt.% of self-prepared MeBz-2-C18 or purchased T406, and the base oil was mixed at 60 ℃ for 2 h.

3.5. Tribological Testing

The tribological behavior of MeBz-2-C18 in base oil was evaluated using a Tenkey MS10A four-ball testing machine (Xiamen Tenkey Automation Co., Ltd., Xiamen, China), which was compared with the commercially available T406. All balls used were made of GCr15 bearing steel with a diameter of 12.7 mm. Following the NB/SH/T 0189-2017[17] standard, tests were conducted at 75°C with a steel ball rotational speed of 1200 rpm and a load of 392 N for 1 hour. Each test was performed at least three times to ensure the reproducibility of the ave. COF and ave. WSD.

4. Conclusions

In this study, methylbenzotriazole and oleic acid were used to synthesize a new methylbenzotriazole-amide derivative (MeBz-2-C18) that possesses active functional amides and long alkyl chains, which was characterized by NMR, HR-MS, FT-IR and TGA. The tribological performance of MeBz-2-C18 in synthetic base oil was investigated and compared with that of the commercial additive T406, and micro-lubrication mechanism of MeBz-2-C18 was uncovered. The main conclusions are as follows:

(1) The introduction of long alkyl chains and amide bonds allows MeBz-2-C18 to exhibit better storage and thermal stability in synthetic base oil compared to the commercial T406, with a residual mass at 300 °C of 89.3% vs. 11.0%.

(2) The optimal addition of MeBz-2-C18 in synthetic base oil is 0.5 wt.%, making the ave. WSD and ave. COF reduced by 21.6% and 3.2%, which is better than thaf of commercial additive T406.

(3) Wear surface analysis and DFT calculations suggest that MeBz-2-C18 has a stronger adsorption on metal surfaces than T406, in which the amide bonds break preferentially during friction,, reducing interfacial shear forces and facilitating the formation of iron oxide films on the metal surface, thus exhibiting good anti-wear and friction-reducing properties.

Supplementary Materials: The following supporting information can be downloaded at Preprints.org: Figure S1 (a) ^{1}H NMR, (b) ^{13}C NMR, (c) HR-MS and (d) FT-IR spectra of MeBz-2-Etn. Figure S2 (a) ^{1}H NMR, (b) ^{13}C NMR, (c) HR-MS and (d) FT-IR spectra of MeBz-2-C18. Figure S3 (a) TG and DTG curves of MeBz-2-Etn、MeBz-2-C18 and T406. Table S1 Storage stability of oil samples with different additions of MeBz-2-C18 and the same addition (0.5 wt.%) of MeBz-2-C18 or T406. Table S2 SEM-EDS analysis of surfaces lubricated with oils before and after tribological tests. Table S3 Surface XPS analysis after friction testing of base oils and oil samples supplemented with 0.5 wt.% MeBz-2-C18.

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